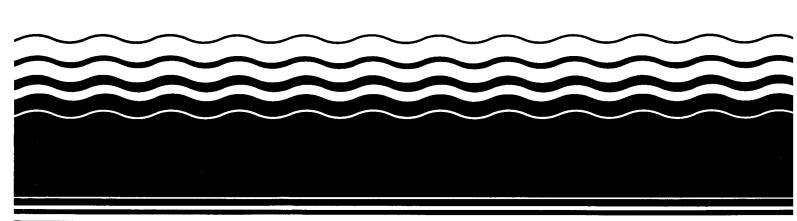
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Superfund

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Subsurface Contamination Reference Guide



SUBSURFACE CONTAMINATION REFERENCE GUIDE

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Chapter 1 INTRODUCTION

Ground water contamination is a significant concern at approximately 70% of the Superfund sites. The difficulties associated with cleaning up contaminated ground water are becoming more and more evident as experience with this problem increases. A recent study of 19 ground water extraction systems (U.S. EPA, 1989, EPA/540/2-89/054) indicated several factors that can limit the effectiveness of the traditional pump-and-treat remediation systems and also identified possible enhancements than may improve the performance of these systems. Many of the factors limiting performance are a result of interactions between the contaminants and the subsurface environments and can be tied to particular contaminant properties (e.g., solubility, density) and/or the nature of the subsurface (e.g., low permeability, fractures).

As a result of the referenced study several recommendations were made including a recommendation to collect more detailed data on the vertical stratigraphy of the subsurface, the vertical variations in contaminant concentration, and the proportion of contaminant sorbed to the soil in the saturated zone. To the extent possible potential limitations should be recognized even before the investigation begins; i.e. during scoping, to better focus remedial investigation/feasibility study (RI/FS) efforts.

This guide was developed to provide a source of information pertaining to important fate and transport properties for a variety of contaminants commonly found in ground water at Superfund sites. This information may help to focus site investigation efforts and identify early-on potential remediation strategies. Knowledge pertaining to the magnitude of these properties can be used to help to project whether contaminants will sorb significantly to soils, dissolve and move with ground water flow, migrate downward as a separate phase, or float on the water table. Potential remedial technologies have been identified for various combinations of contaminant types and hydrogeological environments.

Information pertaining to contaminant fate and transport properties have been presented in tabular form and provided as separately published charts for easy reference.

This document was prepared as a task of the Subsurface Remediation Information Center located at the U.S. EPA Robert S. Kerr Environmental Research Laboratory (RSKERL), Ada, Oklahoma. Questions pertaining to the information contained in this document should be addressed to John E. Matthews at RSKERL-Ada (405/332-8800).

Chapter 2 SUBSURFACE REMEDIAL TECHNOLOGIES

Subsurface remedial technologies which may be applicable at Superfund sites are described below. These descriptions are intended as guidance for use in conjunction with the tabular data presented in separately published charts that are provided with this document (Tables 1 and 2, EPA/540/2-90/011a; Table 3, EPA/540/2-90/011b).

2.1 PUMP AND TREAT

2.1.1 Continuous Pumping

Pump and treat remediation technology is applicable to the saturated zone and refers to the extraction of contaminated ground water from the subsurface and subsequent treatment of the extracted ground water at the surface. Extraction of contaminated ground water is accomplished through the use of extraction (pumping) wells which are completed at specified locations and depths to optimize contaminant recovery. Determination of the locations and depths of extraction wells requires prior delineation of the contaminant plume and knowledge of the aquifer properties. Injection wells may be installed to enhance contaminant recovery by flushing contaminants toward extraction wells.

Pump and treat technology is best suited for managing mobile chemicals (i.e., $\log K_{\infty}$ or $\log K_{\infty}$ values less than 3.0 and 3.5, respectively) residing in relatively permeable and homogeneous hydrogeologic settings. Factors which must be considered and may limit the ability of pump and treat remediation treatment to achieve cleanup concentrations in the ground water include: 1) the presence of chemicals with relatively high K_{∞} or K_{∞} values (e.g. $\log K_{\infty} > 3.0$ or $\log K_{\infty} > 3.5$), 2) aquifers exhibiting low permeability properties (e.g., < 10^{-6} cm/s), 3) highly heterogeneous hydrogeologic settings (e.g. highly stratified aquifers with multiple layers of coarse and fine textured material), and 4) the presence of spatially discontinuous or inaccessible dense non-aqueous phase liquid (DNAPL).

Pump and treat technology may, in many cases, be used to aid in the removal of light non-aqueous phase liquid (LNAPL) and/or DNAPL which may be present. Recovery of LNAPL residing as free product on the surface of the water table, for example, can be facilitated by using pumping wells to create cones of depression. DNAPL residing as large pools in topographical lows at the bottom of aquifers can be recovered by pumping from wells screened over the thickness of the pools. In cases where recovery is not feasible (e.g., DNAPL resides in fractures or is present

as spatially discontinuous free product within an aquifer), alternative measures such as physical containment (e.g. cement-bentonite walls) should be considered.

Pumping technology may also be used as a means of containing or controlling contaminant plumes. This is accomplished through control of hydraulic gradients by selectively locating pumping wells in the area of the plume. Control of hydraulic gradients should be considered in conjunction with physical containment options.

The surface treatment of extracted ground water will vary depending on the contaminants present. Typical actions include air stripping, activated carbon adsorption and biological treatment. In some cases, treated ground water may be amended with nutrients and oxygen and reinjected into the subsurface to aid in stimulating biodegradative processes.

Pump and treat remediation technology generally will play an important role in ground water cleanup. For information regarding applicability of pump and treat technology and its modifications, contact Randall R. Ross at the RSKERL-Ada (405-332-8800).

2.1.2 Pulsed Pumping

Pulsed pumping is a modification of standard pump and treat technology which involves regular or periodic cessation of pumping activities to optimize ground water cleanup. Pulsed pumping may be necessary or more cost-effective in cases where extraction wells can not sustain yields (e.g., in bedrock and unconsolidated deposits of low permeability), where desorption and/or dissolution of contaminants in the subsurface is relatively slow, or where hydraulic conductivity heterogeneity is high. Pulsed pumping may be appropriate for: 1) low yield consolidated and unconsolidated deposits; 2) relatively homogeneous hydrogeologic settings containing contaminants with log K_{∞} values between 2.0 and 4.0 (or log K_{ow} values between 2.5 and 4.5); 3) heterogeneous formations consisting of alternating high and low permeability layers and containing contaminants with log K_{∞} and log K_{ow} values less than 3.0 and 3.5, respectively; and 4) hydrogeological settings containing low to moderately soluble residual non-aqueous phase liquid (NAPL).

A potential concern associated with implementation of pulsed pumping is the uncontrolled migration of the contaminant plume during non-pumping phases. Nearby water supply wells or irrigation systems may significantly impact the behavior of the contaminant plume during non-pumping phases and thereby create a potentially more serious contamination scenario.

2.1.3 Reinjection

Reinjection, which often is used in combination with pump and treat or pulsed pumping, generally refers to injection of treated ground water back into the subsurface. Reinjection may be accomplished through the use of injection wells or other means such as infiltration galleries. Reinjected ground water can be used to help remove contaminants residing in the unsaturated zone by forcing these contaminants towards extraction wells. Reinjection also may be used in the stimulation of biodegradative processes in the saturated zone, thereby enhancing cleanup of the saturated zone. In such cases, the injectate is amended with nutrients and an oxygen source. In special cases, the injectate may be amended with surfactants or other compounds (i.e. chemical extraction) to facilitate removal of adsorbed and residual organics in the unsaturated and/or saturated zones.

2.2 SOIL VACUUM EXTRACTION

Vacuum extraction technology involves the enhanced removal of chemicals in the subsurface through application of a vacuum. The applied vacuum enhances volatilization of compounds from soil and pore water. The technology is particularly applicable to relatively volatile organic compounds (Henry's Law Constant > 10⁻³ atm-m³/mole) residing in the unsaturated zone. The technology also is applicable for removal of volatile light non-aqueous phase liquids (LNAPLs) floating on the water table or entrained in the capillary fringe. The process involves installation of vacuum extraction wells at strategic locations and depths. The spacing of extraction wells is dependent on soil properties such as permeability and porosity. The technology is applicable to most soil types although removal efficiency will generally decrease with decreasing soil permeability and increasing subsurface stratigraphy (heterogeneity).

Vapors released from the subsurface as a result of the vacuum extraction process may be captured and then processed through a liquid-vapor separator. The separated volatile organic vapor fraction may be treated with activated carbon or other means.

Vacuum extraction also can serve a dual purpose by enhancing removal of subsurface organic contaminants through stimulation of aerobic biodegradative processes. This is accomplished by ensuring a constant and ample supply of oxygen for use by indigenous subsurface microbial populations.

Vacuum extraction also may be used in conjunction with in-situ steam extraction (see description below). Steam extraction may enhance the recovery of organic chemicals, including NAPL's, from the vadose zone.

Vacuum extraction is a proven remedial technology which is being increasingly applied at Superfund sites. For further information regarding the applicability of vacuum extraction contact Dominic DiGiulio at the RSKERL-Ada (405-332-8800).

2.2.1 In-Situ Steam Extraction

In-situ steam extraction facilitates the removal of moderately volatile (10⁻³ > v.p. > 10⁺⁰ mm Hg) residual organics, including NAPLs, from the vadose zone. Steam extraction technology utilizes injection of pressured steam to the contaminated horizon to thermally enhance the evaporative rate of the contaminant and its subsequent removal. Injection of steam also can be expected to enhance removal of residual NAPL's in the unsaturated zone by decreasing their viscosities. Steam extraction is an emerging technology that appears promising, particularly if used in conjunction with vacuum extraction.

2.3 SOIL FLUSHING

Soil flushing technology involves the use of extractant solvents to remove organic and/or inorganic contaminants from soils in the subsurface. Extractant solvents may include water, water-surfactant mixtures, acids, bases, chelating agents, oxidizing agents and reducing agents. The extractants used, however, should be limited to those which exhibit low toxicity and will not otherwise adversely impact the subsurface environment. Proper control measures must be exercised to prevent migration of extractant-contaminant mixtures from the vadose zone into ground water.

In-situ soil flushing can be applicable to those compounds residing in the vadose zone which are not amenable to removal by vacuum extraction. These compounds may include semi-volatile organics, cyanide salts, and metals (e.g., selenium, arsenic, and hexavalent chromium). Applications are limited to soils with adequate permeability ($k > 10^{-5}$ cm/s) and a reasonable degree of homogeneity. For semi-volatile organics amenable to biodegradation, bioremediation in concert with in-situ vacuum extraction (or alternative air circulation technology) will likely be a better choice.

The effectiveness of soil flushing relative to other vadose zone remedial technologies is not clear. Due to the potential environmental impact of in-situ soil flushing, the technology should only be used in situations where other remediation technologies of lower potential environmental impact are not appropriate.

Soil flushing has been used at some Superfund sites although the level of its success is not clear. For information regarding the applicability of soil flushing, contact John Brugger at the EPA Risk Reduction Engineering Laboratory, Edison NJ (201-321-6634).

2.3.1 Chemical Extraction

Chemical extraction as used in this document refers to a specialized form of soil flushing that applies only to the saturated zone. This technology involves the use of extractant solvents to enhance desorption or solubilization of contaminants in the saturated zone in conjunction with pump and treat operations. Extracted ground water is amended with solvents and/or other chemicals then reinjected at strategic locations into the aquifer. The extractants used are similar to those used in soil flushing in the vadose zone. Chemical extraction is most applicable in cases where contaminants are not easily mobilized or removed with water alone, i.e., strongly sorbed to aquifer solids or present as residual saturation. Caution should be exercised when using chemical extraction methods, however, because of the potential adverse impact introduced chemicals may have on the subsurface environment.

2.4 CONTAINMENT

Containment technologies are used to isolate contaminated areas in the subsurface from the surrounding uncontaminated environment. Containment usually involves installation of an impermeable barrier around, or a cap over, the affected area. The barrier may take the form of a slurry wall (e.g. soil-bentonite wall or cement-bentonite wall), a grout curtain, or sheet piling cut-offs. In the saturated zone, these barriers must be tied into an impermeable layer at the base of the aquifer. Containment, although not considered a remediation technology, warrants consideration in concert with remedial technologies or as an interim measure while remediation technologies can be considered. Spatially discontinuous DNAPL residing within an aquifer, for example, may be an appropriate scenario for considering containment. The selection of the barrier material must take into account the compatibility of the material with the contaminant(s) in question. Containment also may include installation of a cap over the contaminated area to impede infiltration of water into that area.

Another method of controlling contaminant migration is hydraulic containment. Hydraulic containment involves retardation of movement of a ground water contaminant plume by using pumping wells to control hydraulic gradients. Hydraulic

containment may be used early in a site investigation to prevent plume expansion while a more detailed characterization is completed.

For information regarding the applicability of containment technologies, contact Dr. Walter Grube at the EPA Risk Reduction Engineering Laboratory, Cincinnati, OH (513-569-7798).

2.5 BIOREMEDIATION

Bioremediation technologies involve enhancing biodegradation of contaminants in the saturated and unsaturated zones of the subsurface environment through the artificial stimulation of indigenous soil and ground water microbial populations. Natural biodegradative processes are enhanced by optimizing conditions necessary for subsurface microbes to grow and complete metabolic pathways. Bioremediation is applicable only for treating organic contaminants. Bioremediation should only be considered in conjunction with source control.

Bioremediation for subsurface contamination often can be carried out in situ. The successful execution of an in-situ bioremediation program will depend upon: 1) amenability of the organic compound(s) to biodegradation, 2) permeability and heterogenic properties of the subsurface regime, 3) ability of the delivered oxygen and nutrients to reach the contaminated area, and 4) other factors such as temperature and pH.

In situ bioremediation in the saturated zone can be applied as a specialized form of pump and treat. Extracted ground water from the contaminated zone is treated at the surface, amended with nutrients and oxygen, and then reinjected into the subsurface at strategic locations. Difficulties may arise in the dissemination of oxygen and nutrients in low permeability or highly heterogeneous regimes. Some states may not allow reinjection of treated ground water; therefore, amendments must be delivered to the injection point in clean water.

In situ bioremediation in the unsaturated (vadose) zone can be applied as a specialized form of soil vacuum extraction. The air circulation induced by soil vacuum extraction ensures an ample supply of oxygen to the indigenous microbial population. Other vadose zone in situ bioremediation systems use infiltration galleries or injection wells for delivery of oxygen and nutrients.

Bioremediation is a promising technology for vadose zone soils and contaminated ground waters. For further information regarding the applicability of bioremediation, contact John E. Matthews, Scott G. Huling or John T. Wilson at the RSKERL-Ada (405-332-8800).

2.6 IN-SITU VITRIFICATION

In-situ vitrification (ISV) transforms contaminated soil into an inert glass-like mass that is highly resistant to weathering and leaching. The technique employs electrodes and a high amperage current to heat surrounding soil from 1600 °C to 2000 °C. When operating temperatures are reached a molten mass of contaminated soil is created. As the mass expands it assimilates nonvolatile compounds into its structure and destroys volatile organic compounds by pyrolysis. The technology is generally more applicable at sites having soils contaminated with metals or organic chemicals exhibiting high K_{oc} or K_{ow} values.

In-situ vitrification is a proven technology which has been implemented at selected sites. For further information regarding the applicability of in-situ vitrification, contact Teri Shearer at the EPA Risk Reduction Engineering Laboratory, Cincinnati, OH (513-569-7949).

2.7 TREATMENT COMBINATIONS

Often it will be necessary to implement a combination of treatment technologies to effectively remediate or control subsurface contamination. An example of such a combination is pump and treat with in-situ bioremediation or chemical extraction. One of these combinations may be appropriate at sites where contaminants are strongly adsorbed within the aquifer, and pump and treat alone is expected to have limited success. In-situ bioremediation or chemical extraction could facilitate removal of the strongly sorbed contaminants, thereby enhancing the overall remediation effort. In general, in-situ bioremediation or chemical extraction would be most effective after initial recovery efforts using pump and treat alone have been completed.

Another useful treatment combination involves pump and treat and containment. This combination may be of interest in cases where DNAPL is distributed in a spatially discontinuous manner within the aquifer. Because DNAPL recovery in such a case would be very difficult, the only recourse might be to control and/or contain the contamination. Pump and treat would initially be used to draw in or reduce the size of the aqueous phase contaminant plume generated by the DNAPL. Physical containment would then be used to isolate the DNAPL source area.

An additional treatment combination which may be of interest is aquifer dewatering using pump and treat followed by soil vacuum extraction. This combination of technologies may be of use in cases where an aquifer is

contaminated with volatile organics and dewatering portions of the aquifer is feasible. Pumping would be used to dewater a portion of the aquifer so that vacuum extraction could be applied to enhance volatilization and biodegradation of the volatile organics contaminants in the dewatered zone.

Combinations involving more than two treatment technologies also should be considered in efforts to optimize cleanup of subsurface contamination.

Chapter 3 CONTAMINANT PROPERTIES AFFECTING SUBSURFACE TRANSPORT AND FATE

The following is a description of some important properties which may play an important role in the transport and fate of contaminants in the subsurface. These descriptions are intended to provide guidance for using the tabular information presented in the separately published charts accompanying this document.

- Melting Point The melting point of a compound provides an indication of the physical state of a pure compound at field temperatures. Compounds with melting points above 30°C, for example, would be expected to be immobile in pure form. Such compounds would be of primary concern when in the dissolved phase, either in water or other solvent. Compounds with melting points lower than 30°C may be present as mobile non-aqueous phase liquid.
- Water Solubility Water solubility governs the extent to which a contaminant will partition into the aqueous phase. More soluble contaminants would be expected to migrate further in the subsurface than less soluble compounds. The greater the water solubility of a compound, the greater will be the tendency for that compound to migrate with the aqueous advective flow component. Contaminants with higher water solubilities are more amenable to removal from the saturated zone by pump and treat technology. These same compounds, however, are more likely to migrate through the vadose zone to ground water.
- Vapor Pressure The vapor pressure of a compound provides an indication of the extent to which the compound will volatilize. The tendency of a compound to volatilize will rise proportionately with its vapor pressure. Compounds with higher vapor pressures are more amenable to treatment with vacuum extraction technologies. For comparative purposes, the vapor pressure of water at 20°C is 17.5 mm Hg.
- Henry's Law Constant Henry's Law Constant provides an indication of the extent to which a compound will volatilize from an aqueous solution. Henry's Law Constant is directly proportional to the vapor pressure of the compound and inversely proportional to the water solubility of the compound. The greater the Henry's Law Constant of a compound, the greater will be the tendency of the compound to volatilize from aqueous solution. Compounds with higher Henry's Law Constants are more amenable to treatment with vacuum extraction technologies.

- Density The density of a compound indicates whether the compound is heavier or lighter than water. (The density of water is approximately 1.0 g/cc). Liquid compounds with densities greater than 1.0 g/cc and of only limited water solubility (i.e. DNAPLs), may migrate vertically under the influence of gravity. DNAPLs may eventually gravitate to the bottom or other region of an aquifer where an impermeable layer is encountered. Compounds with limited water solubility and with densities less than 1.0 g/cc will tend to float on the water table.
- Dynamic Viscosity Dynamic viscosity provides an indication of the ease with which a compound (in its pure form) will flow. The mobility of the compound in pure form is inversely proportional to its dynamic viscosity. The dynamic viscosity of water is approximately 1.0 centipoise (cp).
- Kinematic Viscosity The kinematic viscosity of a compound takes into account the density of the compound and provides an indication of the ease with which the compound (in its pure form) will percolate through the subsurface. The lower the kinematic viscosity of a compound, the greater will be its tendency to migrate in a downward direction. Kinematic viscosity is of particular importance with regard to the movement of DNAPLs in aquifers. The lower the kinematic viscosity of a DNAPL, the greater will be the ease with which the DNAPL will move downwards and penetrate the finer grained layers in the subsurface. The kinematic viscosity of water is approximately 1.0 centistokes (cs).
- Octanol/Water Partition Coefficient (K_{ow}) The octanol/water partition coefficient is a measure of the extent to which a contaminant partitions between octanol and water. It is the ratio of the concentration of the compound in octanol to the concentration of the compound in water. The K_{ow} provides an indication of the extent to which a compound will adsorb to a soil or an aquifer solid, particularly organic material. The greater the K_{ow} value of a compound, the greater will be its tendency to be adsorbed in the subsurface.
- Organic Carbon Partition Coefficient (K_∞) The organic carbon partition coefficient is the ratio of the amount of chemical adsorbed per unit weight of organic carbon in the soil to the concentration of the chemical in solution at equilibrium. The K_∞ is similar to the K_∞.
- Bicdegradability Potential The biodegradability potential of a compound is important in determining the feasibility of using bioremediation as a treatment technology. The greater the biodegradability of a compound, the greater will be the susceptibility of the compound to a bioremediation process. Only aerobic biodegradability is addressed in this document.

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